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Synthesis of fullerene–oligophenyleneethynylene hybrids

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Abstract—Disymmetrically substituted oligophenyleneethynylene (OPE) derivatives have been prepared by a new iterative method and attached to C_{60} by a 1,3-dipolar cycloaddition of the azomethine ylides generated in situ from the corresponding OPE aldehydes and sarcosine. © 2001 Published by Elsevier Science Ltd.

Following the observation of photoinduced electron transfer from conjugated polymers to C_{60},[1] a novel approach to the preparation of photovoltaic devices has been proposed by Heeger, Wudl and co-workers.[2] It is based on an interpenetrating blend of donor (conjugated polymer) and acceptor (C_{60}) sandwiched between two asymmetric contacts (two metals with different workfunctions). The performance of this type of device is very sensitive to the morphology of the film.[2] Ideally, an acceptor species should be within the exciton diffusion range from any donor species and vice versa. However, the donor and acceptor molecules are usually chemically incompatible and tend to undergo uncontrolled macrophase separation. In order to avoid any problems arising from bad contacts at the junction, we have recently proposed a new concept: the bicontinuous network can be obtained by chemically linking a hole-conducting oligophenylenevinylene moiety to an electron-conducting fullerene subunit.[3,4] The hybrid compound has been incorporated in a solar cell and a photocurrent was effectively obtained.[3] Even if the efficiencies of the molecular photovoltaic systems are still low, further improvements could be expected by the utilization of new fullerene derivatives. In addition, it is important to highlight that the behavior of a unique molecule in a photovoltaic cell and the study of its electronic properties allows us to obtain easily structure/activity relationships for a better understanding of the photovoltaic system.[4,5] As part of this research, we now report the synthesis of C_{60} derivatives bearing oligo-*para*-phenyleneethynylene (OPE) substituents for future photovoltaic applications. The disymmetrically substituted OPE precursors have been prepared by a new iterative approach,[6,7] using successive Corey–Fuchs dibromoolefination,[8] and treatment with an excess of LDA followed by a metal-catalyzed cross-coupling reaction of the resulting terminal alkyne.

The synthesis of the functionalized OPE derivatives is depicted in Scheme 1. Reaction of hydroquinone with 1-bromooctane in DMF at 80°C in the presence of K_2CO_3, followed by iodination of the resulting 1,4-dioctyloxybenzene, yielded **1** in an overall yield of 57%. Compound **2**, the key building block to this synthesis, was obtained in 85% yield by treatment of **1** with *n*-BuLi (1 equiv.) in Et_2O at 0°C followed by quenching with DMF. Compound **2** was then subjected to a Pd-catalyzed cross-coupling reaction[9] with (triisopropylsilyl)acetylene to give alkynylated **3** in 79% yield. Subsequent treatment with $CBr_4/PPh_3/Zn$ under the conditions described by Corey–Fuchs[8] yielded dibromoolefine **4** in a quantitative yield. Elimination of HBr and halogen–metal exchange was best achieved with an excess of LDA[10] in THF at −78°C and the resulting anion was quenched with NH_4Cl to give mono-protected bisalkyne **5** in 91% yield. The OPE dimer **6** was then obtained in 69% yield by Pd-catalyzed cross-coupling between **2** and **5**. Dibromoolefination according to Corey–Fuchs provided the desired intermediate which after treatment with an excess of LDA in THF at −78°C and quenching with NH_4Cl afforded **7**. Finally, compound **7** was subjected to a Pd-catalyzed cross-coupling reaction with **2** to yield the OPE trimer **8**. This new iterative methodology for the synthesis of disymmetrically substituted OPE derivatives appears to be an interesting alternative to the approaches reported by the groups of Tour[7a] and Godt.[7b] On the one hand, compared to the strategy based on the trimethylsilyl and the 3,3-diethyltriazene functions as complementary

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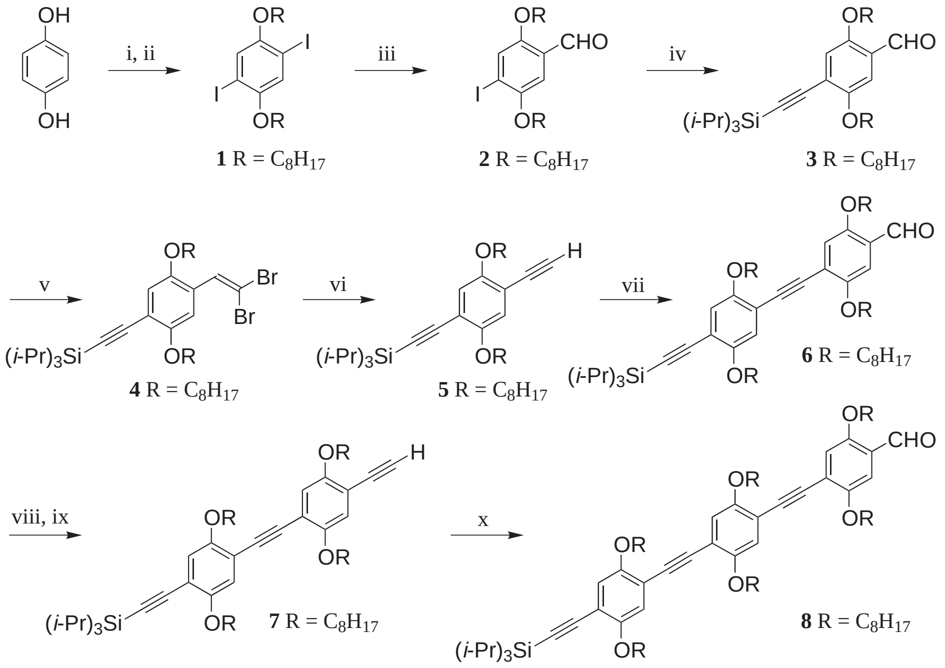
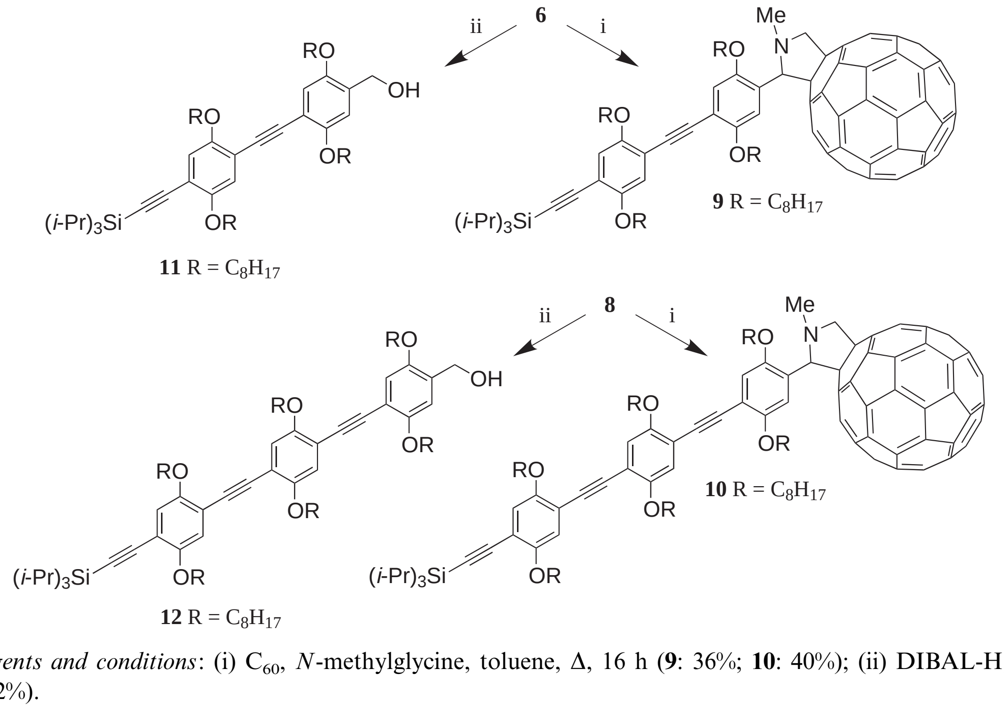


Scheme 1. *Reagents and conditions*: (i) 1-bromooctane, K_2CO_3, DMF, 80°C, 24 h (90%); (ii) I_2, KIO_3, H_2SO_4, CH_3CO_2H, 80°C, 12 h (63%); (iii) *n*-BuLi (1 equiv.), Et_2O, 0°C, 15 min., then DMF, 0°C to rt, 2 h (85%); (iv) (triisopropylsilyl)acetylene, $PdCl_2(PPh_3)_2$, CuI, Et_3N, rt, 24 h (79%); (v) CBr_4, PPh_3, Zn, CH_2Cl_2, 0°C to rt, 12 h (99%); (vi) LDA, THF, −78°C, then aqueous NH_4Cl (91%); (vii) **2**, $PdCl_2(PPh_3)_2$, CuI, Et_3N, rt, 24 h (69%); (viii) CBr_4, PPh_3, Zn, CH_2Cl_2, 0°C to rt, 12 h (99%); (ix) LDA, THF, −78°C, then aqueous NH_4Cl (92%); (x) **2**, $PdCl_2(PPh_3)_2$, CuI, Et_3N, rt, 24 h (77%).

protecting groups for terminal alkyne and aryl iodine,[7a] respectively, it avoids the use of large amounts of rather volatile carcinogenic methyl iodide. On the other hand, compared to the strategy based on the bromine–iodine selectivity of the Pd-catalyzed alkyne–aryl coupling[7b] which is not always completely iodo-selective, it prevents the formation of undesirable symmetric byproducts.

The preparation of the fullerene–OPE hybrids **9** and **10** is depicted in Scheme 2. The functionalization of C_{60} is based on the 1,3-dipolar cycloaddition of the azomethine ylide generated in situ from the corresponding aldehyde and *N*-methylglycine.[11] In a typical procedure, a solution of the OPE aldehyde **6** (350 mg), C_{60} (308 mg) and *N*-methylglycine (208 mg) in toluene (300 ml) was refluxed under argon for 16 h. After cooling,



Scheme 2. *Reagents and conditions*: (i) C_{60}, *N*-methylglycine, toluene, Δ, 16 h (**9**: 36%; **10**: 40%); (ii) DIBAL-H, THF, 0°C, 2 h (**11**: 99%; **12**: 92%).

the resulting solution was evaporated to dryness and column chromatography (SiO_2, toluene/hexane 4:1) yielded **9** (230 mg, 36%). Compound **10** was obtained under similar conditions from **8**, C_{60} and sarcosine. In addition, compounds **11** and **12**, which were used as reference compounds for the absorption and emission properties of the corresponding C_{60}-OPE derivatives were prepared by DIBAL-H reduction of **6** and **8**, respectively.

The C_{60}-OPE derivatives **9** and **10** were characterized by ^1H and ^{13}C NMR, FAB-MS and elemental analyses.[12] The UV–vis spectrum of both **9** and **10** corresponds to the sum of the spectra of their two components indicating that there are no significant ground state interactions between the two chromophores. As depicted in Fig. 1, the absorption spectrum of **9** recorded in CH_2Cl_2 shows the characteristic bands of a fulleropyrrolidine derivative at 430 and 702 nm as well as the diagnostic OPE band at 365 nm. The UV–vis spectrum of the higher homologue **10** is similar but due to the increased length of the π-conjugated system, the absorption maximum of the OPE moiety is shifted to 392 nm. Preliminary luminescence measurements show a strong quenching of the OPE fluorescence by the fullerene moiety in both **9** and **10** indicating the occurrence of intramolecular photoinduced processes. Detailed photophysical studies are currently under investigation in collaboration with the Armaroli group (Bologna, Italy) and special emphasis is placed on the detection of photo-induced and long-lived charge-separated states.

A new iterative approach for the synthesis of disymmetrically substituted OPE derivatives has been developed. This enables us to prepare building blocks for the construction of C_{60}-OPE derivatives which present all the characteristic features required for photovoltaic applications. Incorporation of compounds **9** and **10** in devices is now under investigation for solar energy conversion in collaboration with the Hadziioannou group (Groningen, The Netherlands).

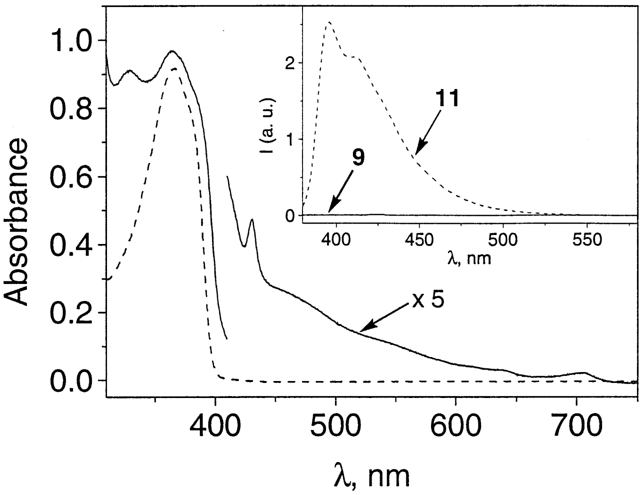


Figure 1. Absorption spectra of **9** (full line) and **11** (dashed line). Inset: fluorescence spectra of optically matched solutions of **9** (full line) and **11** (dashed line); $\lambda_{exc} = 365$ nm. All the experiments were carried out in CH_2Cl_2 solutions at 298 K.

Acknowledgements

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References

1. Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. *Science* **1992**, *258*, 1474–1476.
2. Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789–1791.
3. Nierengarten, J.-F.; Eckert, J.-F.; Nicoud, J.-F.; Ouali, L.; Krasnikov, V.; Hadziioannou, G. *Chem. Commun.* **1999**, 617–618.
4. Eckert, J.-F.; Nicoud, J.-F.; Nierengarten, J.-F.; Liu, S.-G.; Echegoyen, L.; Barigelletti, F.; Armaroli, N.; Ouali, L.; Krasnikov, V.; Hadziioannou, G. *J. Am. Chem. Soc.* **2000**, *122*, 7467–7479.
5. Peeters, E.; van Hal, P. A.; Knol, J.; Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C.; Janssen, R. A. J. *J. Phys. Chem. B* **2000**, *104*, 10174–10190.
6. For reviews on π-conjugated systems, see: (a) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537–554; (b) Müllen, K.; Wegner, G. *Electronic Materials: The Oligomer Approach;* Wiley–VCH: Weinheim, 1998; (c) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1351–1377; (d) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605–1644; (e) Tour, J. M. *Acc. Chem. Res.* **2000**, *33*, 791–804.
7. (a) Schumm, J. S.; Pearson, D. L.; Tour, J. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1360–1363; (b) Ziener, U.; Godt, A. *J. Org. Chem.* **1997**, *62*, 6137–6143.
8. Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, *13*, 3769–3772.
9. (a) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Nagihara, N. *Synthesis* **1980**, *00*, 627–630; (b) *Metal-catalyzed Cross-coupling Reactions*; Diederich, F.; Stang, P. J., Eds.; Wiley–VCH: Weinheim, 1998.
10. (a) Nierengarten, J.-F.; Schreiber, M.; Diederich, F.; Gramlich, V. *New J. Chem.* **1996**, *20*, 1273–1284; (b) Solladié, N.; Gross, M. *Tetrahedron Lett.* **1999**, *40*, 3359–3362.
11. Prato, M.; Maggini, M. *Acc. Chem. Res.* **1998**, *31*, 519–526.
12. Spectroscopic data for **9**: brown solid (mp 124°C); ^1H NMR (200 MHz, $CDCl_3$): 7.58 (s, 1H), 7.03 (s, 1H), 6.93 (s, 1H), 6.92 (s, 1H), 5.54 (s, 1H), 4.98 (d, *J* 9.5 Hz, 1H), 4.32 (d, *J* 9.5 Hz, 1H), 4.18–3.67 (m, 8H), 2.83 (s, 3H), 1.86–1.73 (m, 8H), 1.58–1.28 (m, 40H), 1.14 (s, 21 H), 0.88–0.84 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$): 156.57, 154.97, 154.27, 154.03, 154.00, 153.71, 153.12, 151.43,

147.25, 146.69, 146.57, 146.22, 146.18, 146.14, 146.06, 146.02, 145.90, 145.68, 145.52, 145.41, 145.25, 145.19, 145.07, 144.56, 144.50, 144.42, 144.29, 143.00, 142.95, 142.63, 142.59, 142.51, 142.23, 142.20, 142.09, 142.04, 141.91, 141.69, 141.58, 140.13, 140.08, 139.65, 139.39, 136.39, 136.20, 136.07, 134.53, 127.12, 117.77, 116.41, 116.14, 114.72, 114.32, 113.75, 113.33, 102.99, 96.35, 91.33, 90.42, 76.48, 75.59, 69.97, 69.73, 69.19, 69.13, 68.58, 40.13, 31.88, 31.85, 31.82, 29.50, 29.45, 29.37, 29.28, 26.18, 26.04, 26.01, 25.91, 22.74, 22.67, 18.68, 14.18, 14.12, 14.09, 11.34; FAB-MS: 1646.7 ([*M*+H]$^+$, calcd for $C_{120}H_{100}NO_4Si$: 1646.74), 925.8 ([*M*–C_{60}]$^+$, calcd for $C_{60}H_{99}NO_4Si$: 925.73), 720.2 ($C_{60}{}^+$, calcd for C_{60}: 720.00). Anal. calcd for $C_{120}H_{99}NO_4Si$: C, 87.50; H, 6.06; found: C, 87.69; H, 6.19. For **10**: brown solid. (mp 108°C); ^{1}H NMR (200 MHz, $CDCl_3$): 7.59 (s, 1H), 7.04 (s, 1H), 6.99 (s, 2H), 6.93 (s, 2H), 5.55 (s, 1H), 4.98 (d, *J* 9.5 Hz, 1H), 4.32 (d, *J* 9.5 Hz, 1H), 4.15–3.72 (m, 12H), 2.84 (s, 3H), 1.86–1.71 (m, 12H), 1.57–1.28 (m, 60H), 1.15 (s, 21H), 0.89–0.85 (m, 18H); ^{13}C NMR (50 MHz, $CDCl_3$): 156.50, 154.92, 154.28, 153.96, 153.61, 153.39, 153.15, 151.41, 147.18, 146.61, 146.53, 146.11, 146.06, 146.02, 145.84, 145.62, 145.46, 145.33, 145.20, 145.12, 145.01, 144.50, 144.44, 144.34, 144.24, 142.94, 142.90, 142.57, 142.52, 142.44, 142.19, 142.14, 142.03, 141.98, 141.85, 141.63, 141.53, 140.08, 140.05, 139.60, 139.35, 136.33, 136.17, 135.99, 134.49, 127.12, 117.87, 117.19, 117.08, 117.05, 116.38, 116.22, 116.16, 114.75, 114.35, 114.24, 114.11, 113.86, 113.38, 102.99, 96.37, 91.57, 91.53, 91.34, 90.42, 76.45, 75.59, 75.54, 69.94, 69.77, 69.57, 69.14, 69.11, 68.54, 40.08, 31.85, 31.82, 29.44, 29.39, 29.34, 29.26, 26.17, 25.98, 25.93, 22.70, 22.64, 18.67, 14.17, 14.10, 14.05, 11.33; FAB-MS: 2003.9 ([*M*+H]$^+$, calcd for $C_{144}H_{136}NO_6Si$: 2003.01), 1282.9 ([*M*–C_{60}]$^+$, calcd for $C_{84}H_{135}NO_6Si$: 1282.01), 720.0 ($C_{60}{}^+$, calcd for C_{60}: 720.00). Anal. calcd for $C_{144}H_{135}NO_6Si$: C, 86.32; H, 6.79; found: C, 86.58; H, 6.87.